

PREPARATION OF COMPONENTS FOR REFINERY BLENDING OF TRANSPORTATION FUELS

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BACKGROUND OF THE INVENTION

It is well known that internal combustion engines have revolutionized transportation following their invention during the last decades of the 19th century. While others, including Benz and Gottlieb Wilhelm Daimler, invented and developed engines using electric ignition of fuel such as gasoline, Rudolf
10 C. K. Diesel invented and built the engine named for him which employs compression for auto-ignition of the fuel in order to utilize low-cost organic fuels. Development of improved diesel engines for use in transportation has preceded hand-in-hand with improvements in diesel fuel compositions. Modern high performance diesel engines demand ever more advanced
15 specification of fuel compositions, but cost remains an important consideration.

At the present time most fuels for transportation are derived from natural petroleum. Indeed, petroleum as yet is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. While compositions of natural petroleum or crude oils are significantly varied, all crudes contain
20 sulfur compounds and most contain nitrogen compounds which may also contain oxygen, but oxygen content of most crude is low. Generally, sulfur concentration in crude is less than about 8 percent, with most crude having sulfur concentrations in the range from about 0.5 to about 1.5 percent. Nitrogen concentration is usually less than 0.2 percent, but it may be as high
25 as 1.6 percent.

Crude oil seldom is used in the form produced at the well, but is converted in oil refineries into a wide range of fuels and petrochemical feedstocks. Typically fuels for transportation are produced by processing and blending of distilled fractions from the crude to meet the particular end use
30 specifications. Because most of the crudes available today in large quantity are high in sulfur, the distilled fractions must be desulfurized to yield products which meet performance specifications and/or environmental standards.

Sulfur containing organic compounds in fuels continues to be a major source of environmental pollution. During combustion they are converted to sulfur oxides which, in turn, give rise to sulfur oxyacids and, also, contribute to particulate emissions.

5 Even in newer, high performance diesel engines combustion of conventional fuel produces smoke in the exhaust. Oxygenated compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most such compounds have high vapor
10 pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality, as indicated by their cetane numbers. Furthermore, other methods of improving diesel fuels by chemical hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel pumps, injectors and other
15 moving parts which come in contact with the fuel under high pressures.

 Distilled fractions used for fuel or a blending component of fuel for use in compression ignition internal combustion engines (diesel engines) are middle distillates that usually contain from about 1 to 3 percent by weight sulfur. In the past a typical specification for diesel fuel was a maximum of 0.5
20 percent by weight. By 1993 legislation in Europe and United States limited sulfur in diesel fuel to 0.3 weight percent. By 1996 in Europe and United States, and 1997 in Japan, maximum sulfur in diesel fuel was reduced to no more than 0.05 weight percent. This world-wide trend must be expected to continue to even lower levels for sulfur.

25 The US Environmental Protection Agency is targeting a level of sulfur less than 15 ppm in 2006 for on-road diesel. The European Union specification will be less than 50 ppm in 2005. Further the World Wide Fuels Charter as supported by all global automobile manufacturers proposes even more stringent sulfur requirements of 5 to 10 ppm for the Category IV fuels for
30 "advanced" countries. In order to comply with these regulations for ultra-low sulfur content fuels, refiners will have to make fuels having even lower sulfur levels at the refinery gate. Thus refiners are faced with the challenge of

reducing the sulfur levels in fuels and in particular diesel fuel within the timeframes prescribed by the regulatory authorities.

5 In one aspect, pending introduction of new emission regulations in California and other jurisdictions has prompted significant interest in catalytic exhaust treatment. Challenges of applying catalytic emission control for the diesel engine, particularly the heavy-duty diesel engine, are significantly different from the spark ignition internal combustion engine (gasoline engine) due to two factors. First, the conventional three way catalyst (TWC) catalyst is ineffective in removing NOx emissions from diesel engines, and second, the
10 need for particulate control is significantly higher than with the gasoline engine.

Several exhaust treatment technologies are emerging for control of diesel engine emissions, and in all sectors the level of sulfur in the fuel affects efficiency of the technology. Sulfur is a catalyst poison that reduces catalytic activity. Furthermore, in the context of catalytic control of diesel emissions,
15 high fuel sulfur also creates a secondary problem of particulate emission, due to catalytic oxidation of sulfur and reaction with water to form a sulfate mist. This mist is collected as a portion of particulate emissions.

Compression ignition engine emissions differ from those of spark ignition engines due to the different method employed to initiate combustion.
20 Compression ignition requires combustion of fuel droplets in a very lean air/fuel mixture. The combustion process leaves tiny particles of carbon behind and leads to significantly higher particulate emissions than are present in gasoline engines. Due to the lean operation the CO and gaseous hydrocarbon emissions are significantly lower than the gasoline engine.
25 However, significant quantities of unburned hydrocarbon are adsorbed on the carbon particulate. These hydrocarbons are referred to as SOF (soluble organic fraction).

While an increase in combustion temperature can reduce particulate, this leads to an increase in NOx emission by the well-known Zeldovitch
30 mechanism. Thus, it becomes necessary to trade off particulate and NOx emissions to meet emissions legislation.

Available evidence strongly suggests that ultra-low sulfur fuel is a significant technology enabler for catalytic treatment of diesel exhaust to control emissions. Fuel sulfur levels of below 15 ppm, likely, are required to

achieve particulate levels below 0.01 g/bhp-hr. Such levels would be very compatible with catalyst combinations for exhaust treatment now emerging, which have shown capability to achieve NO_x emissions around 0.5 g/bhp-hr. Furthermore, NO_x trap systems are extremely sensitive to fuel sulfur and
5 available evidence suggests that they would need sulfur levels below 10 ppm to remain active.

In the face of ever-tightening sulfur specifications in transportation fuels, sulfur removal from petroleum feedstocks and products will become increasingly important in years to come.

10 Conventional hydrosulfurization (HDS) catalysts can be used to remove a major portion of the sulfur from petroleum distillates for the blending of refinery transportation fuels, but they are not efficient for removing sulfur from compounds where the sulfur atom is sterically hindered as in multi-ring aromatic sulfur compounds. This is especially true where the sulfur
15 heteroatom is doubly hindered (e.g., 4,6-dimethyldibenzothiophene). These hindered dibenzothiophenes predominate at low sulfur levels such as 50 to 100 ppm and would require severe process conditions to be desulfurized. Using conventional hydrosulfurization catalysts at high temperatures would cause yield loss, faster catalyst coking, and product quality deterioration (e.g.,
20 color). Using high pressure requires a large capital outlay.

In order to meet stricter specifications in the future, such hindered sulfur compounds will also have to be removed from distillate feedstocks and products. There is a pressing need for economical removal of sulfur from distillates and other hydrocarbon products.

25 The art is replete with processes to remove sulfur from distillate feedstocks and products. One known method involves the oxidation of petroleum fractions containing at least a major amount of material boiling above very high-boiling hydrocarbon materials (petroleum fractions containing at least a major amount of material boiling above about 550° F.) followed by
30 treating the effluent containing the oxidized compounds at elevated temperatures to form hydrogen sulfide (500° F. to 1350° F.) and/or hydroprocessing to reduce the sulfur content of the hydrocarbon material. See, for example, U.S. Patent No. 3,847,798 (Jin Sun Yoo, et al) and U.S. Patent No. 5,288,390 (Vincent A. Durante). Such methods have proven to be

of only limited utility since only a rather low degree of desulfurization is achieved. In addition, substantial loss of valuable products may result due to cracking and/or coke formation during the practice of these methods. Therefore, it would be advantageous to develop a process which gives an
5 increased degree of desulfurization while decreasing cracking or coke formation.

Several different oxygenation methods for improving fuels have also been described in the past. For example, U.S. Patent No. 2,521,698 (G. H. Denison, Jr. et al.) describes a partial oxidation of hydrocarbon fuels as
10 improving cetane number. This patent suggests that the fuel should have a relatively low aromatic ring content and a high paraffinic content. U.S. Patent No. 2,912,313 (James B. Hinkamp et al.) states that an increase in cetane number is obtained by adding both a peroxide and a dihalo compound to middle distillate fuels. U.S. Patent No. 2,472,152 (Adalbert Farkas et al.)
15 describes a method for improving the cetane number of middle distillate fractions by the oxidation of saturated cyclic hydrocarbon or naphthenic hydrocarbons in such fractions to form naphthenic peroxides. This patent suggests that the oxidation may be accelerated in the presence of an oil-soluble metal salt as an initiator, but is preferably carried out in the presence of
20 an inorganic base. However, the naphthenic peroxides formed are deleterious gum initiators. Consequently, gum inhibitors such as phenols, cresols and cresylic acids must be added to the oxidized material to reduce or prevent gum formation. These latter compounds are toxic and carcinogenic.

U.S. Patent No. 4,494,961 (Chaya Venkat et al.) relates to improving
25 the cetane number of raw, untreated, highly aromatic, middle distillate fractions having a low hydrogen content by contacting the fraction at a temperature of from 50°C to 350°C and under mild oxidizing conditions in the presence of a catalyst which is either (i) an alkaline earth metal permanganate, (ii) an oxide of a metal of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB or VIIIB of the periodic
30 table, or a mixture of (i) and (ii). European Patent Application 0 252 606 A2 also relates to improving the cetane rating of a middle distillate fuel fraction which may be hydro-refined by contacting the fraction with oxygen or oxidant, in the presence of catalytic metals such as tin, antimony, lead, bismuth and transition metals of Groups IB, IIB, VB, VIB, VIIB and VIIIB of the periodic

table, preferably as an oil-soluble metal salt. The application states that the catalyst selectively oxidizes benzylic carbon atoms in the fuel to ketones.

U.S. Patent No. 4,723,963 (William F. Taylor) suggests that cetane number is improved by including at least 3 weight percent oxygenated aromatic compounds in middle distillate hydrocarbon fuel boiling in the range of 160°C to 400°C. This patent states that the oxygenated alkylaromatics and/or oxygenated hydroaromatics are preferably oxygenated at the benzylic carbon proton.

U.S. Patent No. 6,087,544 (Robert J. Wittenbrink et al.) relates to processing a distillate feedstream to produce distillate fuels having a level of sulfur below the distillate feedstream. Such fuels are produced by fractionating a distillate feedstream into a light fraction, which contains only from about 50 to 100 ppm of sulfur, and a heavy fraction. The light fraction is hydrotreated to remove substantially all of the sulfur therein. The desulfurized light fraction, is then blended with one half of the heavy fraction to product a low sulfur distillate fuel, for example 85 percent by weight of desulfurized light fraction and 15 percent by weight of untreated heavy fraction reduced the level of sulfur from 663 ppm to 310 ppm. However, to obtain this low sulfur level only about 85 percent of the distillate feedstream is recovered as a low sulfur distillate fuel product.

U.S. Patent Application Publication No. 2002/0035306 A1 (Gore et al.) discloses a multi-step process for desulfurizing liquid petroleum fuels that also removes nitrogen-containing compounds and aromatics. The process steps are thiophene extraction; thiophene oxidation; thiophene-oxide and dioxide extraction; raffinate solvent recovery and polishing; extract solvent recovery; and recycle solvent purification.

The Gore et al. process seeks to remove 5-65% of the thiophenic material and nitrogen-containing compounds and parts of the aromatics in the feedstream prior to the oxidation step. While the presence of aromatics in diesel fuel tends to suppress cetane, the Gore et al. process requires an end use for the extracted aromatics. Further, the presence of an effective amount of aromatics serves to increase the fuel density (Btu/gal) and enhance the cold flow properties of diesel fuel. Therefore it is not prudent to extract an inordinate amount of the aromatics.

With respect to the oxidation step, the oxidant is prepared in situ or is previously formed. Operating conditions include a molar ratio of H_2O_2 to S between about 1:1 and 2.2:1; acetic acid content between about 5 and 45% of feed, solvent content between 10 and 25% of feed, and a catalyst volume of less than about 5,000 ppm sulfuric acid, preferably less than 1,000 ppm. Gore et al. also discloses the use of an acid catalyst in the oxidation step, preferably sulfuric acid. The use of sulfuric acid as an oxidizing acid is problematic in that corrosion is a concern when water is present and hydrocarbons can be sulfonated when a little water is present.

According to Gore et al. the purpose of the thiophene-oxide and dioxide extraction step is to remove more than 90% of the various substituted benzo- and dibenzo thiophene-oxides and N-oxide compounds plus a fraction of the aromatics with an extracting solvent that is aqueous acetic acid with one or more co-solvents.

U.S. Patent No. 6,368,495 B1 (Kocal et al.) also discloses a multi-step process for the removal of thiophenes and thiophene derivatives from petroleum fractions. This subject process involves the steps of contacting a hydrocarbon feed stream with an oxidizing agent followed by the contact of the oxidizing step effluent with a solid decomposition catalyst to decompose the oxidized sulfur-containing compounds thereby yielding a heated liquid stream and a volatile sulfur compound. The subject patent discloses the use of oxidizing agents such as alkyl hydroperoxides, peroxides, percarboxylic acids, and oxygen.

WO 02/18518 A1 (Rappas et al) discloses a two-stage desulfurization process which is utilized downstream of a hydrotreater. The process involves an aqueous formic acid based, hydrogen peroxide biphasic oxidation of a distillate to convert thiophenic sulfur to corresponding sulfones. During the oxidation process, some sulfones are extracted into the oxidizing solution. These sulfones are removed from the hydrocarbon phase by a subsequent phase separation step. The hydrocarbon phase containing remaining sulfones is then subjected to a liquid-liquid extraction or solid adsorption step.

The use of formic acid in the oxidation step is not advisable. Formic acid is relatively more expensive than acetic acid. Further, formic acid is considered a "reducing" solvent and can hydride certain metals thereby

weakening them. Therefore, exotic alloys are required to handle formic acid. These expensive alloys would have to be used in the solvent recovery section and storage vessels. The use of formic acid also necessitates the use of high temperatures for the separation of the hydrocarbon phase from the aqueous oxidant phase in order to prevent the appearance of a third precipitated solid phase. It is believed this undesirable phase can be formed due to the poor lipophilicity of formic acid. Therefore at lower temperatures, formic acid cannot maintain in solution some of the extracted sulfones.

U.S. Patent No. 6,171,478 B1 (Cabrera et al.) discloses yet another complex multi-step desulfurization process. Specifically, the process involves a hydrodesulfurization step, an oxidizing step, a decomposition step, and a separation step wherein a portion of the sulfur-oxidated compounds are separated from the effluent stream of the decomposition step. The aqueous oxidizing solution used in the oxidizing step preferably contains acetic acid and hydrogen peroxide. Any residual hydrogen peroxide in the oxidizing step effluent is decomposed by contacting the effluent with a decomposition catalyst.

The separation step is carried out with a selective solvent to extract the sulfur-oxidated compounds. Per the teachings of Cabrera et al. the preferred selective solvents are acetonitrile, dimethyl formamide, and sulfolane.

A number of solvents have been proposed for removing the oxidized sulfur compounds. For example, in U.S. Patent No. 6,160,193 (Gore) teaches the use of a wide variety of solvents suitable for use in the extraction of sulfones. The preferred solvent is Dimethylsulfoxide (DMSO).

A study of a similar list of solvents used in the extraction of sulfur compounds was published by Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. "Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction" *Energy & Fuels* 2000, 14, 1232. That list is displayed below:

N,N-Dimethylformamide (DMF)
Methanol
Acetonitrile
Sulfolane

Gore states that there is a relationship between the solvent's polarity with the solvent's extraction efficiency. All of the solvents listed in the patent and the paper are desirably immiscible with the diesel. They are all characterized as either polar protic or aprotic solvents.

5 WO 01/32809 discloses another process for selectively oxidizing distillate fuel or middle distillates. The subject reference discloses that oxidized distillate fuels such that hydroxyl and or carbonyl groups are chemically bound to paraffinic molecules in the fuel results in a reduction in particulates generated upon combustion of the fuel versus unoxidized fuel. The reference
10 discloses a process for selectively oxidizing saturated aliphatic or cyclic compounds in the fuel using in the presence of various titanium containing silicon based zeolites with peroxides, ozone or hydrogen peroxide such that hydroxyl or carbonyl groups are formed.

U.S. Patent No. 6,402,939 B1 (Yen et al.) discloses a process for the
15 oxidative desulfurization of fossil fuels using ultrasound. Briefly liquid fossil fuel is combined with an acidic aqueous solution comprising water and an hydroperoxide to form a multiphase reaction mixture followed by applying ultrasound to the multiphase reaction medium for a time sufficient to cause oxidation of sulfides to sulfones with are subsequently extracted.

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U.S. Patent Application Publication No. 2001/0015339 A1 (Sherman) discloses a method of removing sulfur compounds from diesel fuel that involves forming oxidizing gas into sub micron size bubbles and dispersing these bubbles into flowing diesel fuel to oxidize the sulfur compounds into
25 sulfoxides and/or sulfones.

In view of the above, it is clear that there is a need for a less complex, economic distillate or diesel desulfurization process that does not employ expensive "severe" hydrotreating technologies involving greater hydrogen
30 useage and substantial capital outlay or oxidation technologies that employ the use of expensive chemical oxidizing agents and avoids the attendant complex handling issues.

The present invention provides for a relatively simple process wherein a distillate feedstock is contacted with an oxygen-containing gas at oxidation conditions in the presence of a heterogeneous catalyst comprising a Group VIII metal on a basic support.

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SUMMARY OF THE INVENTION

The process of the present invention involves reducing the sulfur and/or nitrogen content of a distillate feedstock to produce a refinery transportation fuel or blending components for refinery transportation fuel by contacting the feedstock with an oxygen-containing gas in an oxidation zone at oxidation conditions in the presence of an oxidation catalyst comprising a Group VIII metal and a basic support to form an oxidation zone effluent stream containing oxidized sulfur-containing and/or nitrogen-containing compounds. The oxidized sulfur-containing and/or nitrogen-containing compounds are then separated from the oxidation zone effluent stream by conventional means known to those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

Suitable feedstocks generally include refinery distillate streams boiling at a temperature range from about 50°C to about 650°C, preferably 150°C to about 400°C, and more preferably between about 175°C and about 375°C at atmospheric pressure for best results. These streams include, but are not limited to, virgin light middle distillate, virgin heavy middle distillate, fluid catalytic cracking process light catalytic cycle oil, coker still distillate, hydrocracker distillate, jet fuel, vacuum distillates, and the collective and individually hydrotreated embodiments of these streams. These streams further include the collective and individually hydrotreated embodiments of fluid catalytic cracking process, light catalytic cycle oil, coker still distillate, and hydrocracker distillate.

It is also anticipated that one or more of the above distillate streams can be combined for use as feedstock to the process of the invention. In many cases performance of the refinery transportation fuel or blending components for refinery transportation fuel obtained from the various alternative feedstocks may be comparable. In these cases, logistics such as the volume availability

of a stream, location of the nearest connection and short-term economics may be determinative as to what stream is utilized.

In one aspect, this invention provides for the production of refinery transportation fuel or blending components for refinery transportation fuel from a hydrotreated petroleum distillate. Such a hydrotreated distillate is prepared by hydrotreating a petroleum distillate material boiling between about 50°C and about 650°C by a process which includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate; optionally fractionating the hydrotreated petroleum distillate by distillation to provide at least one low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction, and a high-boiling feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction. In accordance with one embodiment of the process of the present invention the hydrotreated distillate or the low-boiling component can be used as suitable feedstocks for the process of the present invention.

Generally, useful hydrogenation catalysts comprise at least one active metal, selected from the group consisting of the d-transition elements in the Periodic Table, each incorporated onto an inert support in an amount of from about 0.1 percent to about 30 percent by weight of the total catalyst. Suitable active metals include the d-transition elements in the Periodic Table elements having atomic number in from 21 to 30, 39 to 48, and 72 to 78.

The catalytic hydrogenation process may be carried out under relatively mild conditions in a fixed, moving, fluidized or ebullated bed of catalyst. Preferably a fixed bed or plurality of fixed beds of catalyst is used under conditions such that relatively long periods elapse before regeneration becomes necessary, for example an average reaction zone temperature of from about 200°C to about 450°C, preferably from about 250°C to about 400°C, and most preferably from about 275°C to about 350°C for best results, and at a pressure within the range of from about 6 to about 160 atmospheres.

Hydrogen circulation rates generally range from about 500 SCF/Bbl to about 20,000 SCF/Bbl, preferably from about 2,000 SCF/Bbl to about 15,000 SCF/Bbl, and most preferably from about 3,000 to about 13,000 SCF/Bbl for best results.

The hydrogenation process typically operates at a liquid hourly space velocity of from about 0.2 hr⁻¹ to about 10.0 hr⁻¹, preferably from about 0.5 hr⁻¹ to about 3.0 hr⁻¹, and most preferably from about 1.0 hr⁻¹ to about 2.0 hr⁻¹ for best results. Excessively high space velocities will result in reduced overall hydrogenation.

As mentioned above further reduction of heteroaromatic sulfur-containing species from a distillate petroleum fraction by hydrotreating would require that the stream be subjected to very severe catalytic hydrogenation in order to convert these compounds into hydrocarbons and hydrogen sulfide (H₂S). Typically, the larger any hydrocarbon moiety is, the more difficult it is to hydrogenate the sulfur-containing hydrocarbon. Therefore, the residual organo-sulfur compounds remaining after a hydrotreatment are the larger and most structurally hindered heteroaromatics.

Where the feedstock is a high-boiling distillate fraction derived from hydrogenation of a refinery stream, the refinery stream can be a material boiling between about 200°C and about 425°C. Preferably the refinery stream can be a material boiling between about 250°C and about 400°C, and more preferably a material boiling between about 275°C and about 375°C.

Useful distillate fractions can be any one, several, or all refinery streams boiling in a range from about 50°C to about 425°C, preferably 150°C to about 400°C, and more preferably between about 175°C and about 375°C at atmospheric pressure. The lighter hydrocarbon components in the distillate product are generally more profitably recovered to gasoline and the presence of these lower boiling materials in distillate fuels is often constrained by distillate fuel flash point specifications. Heavier hydrocarbon components boiling above 400°C are generally more profitably processed as fluid catalytic cracker feed and converted to gasoline. The presence of heavy hydrocarbon components in distillate fuels is further constrained by distillate fuel end point specifications.

The distillate fractions for the present invention can comprise high and low sulfur virgin distillates derived from high- and low-sulfur crudes, coker distillates, catalytic cracker light and heavy catalytic cycle oils, and distillate boiling range products from hydrocracker and resid hydrotreater facilities.

Generally, coker distillate and the light and heavy catalytic cycle oils are the most highly aromatic feedstock components, ranging as high as 80 percent by weight. The majority of coker distillate and cycle oil aromatics are present as mono-aromatics and di-aromatics with a smaller portion present as tri-aromatics. Virgin stocks such as high and low sulfur virgin distillates are lower in aromatics content typically ranging as high as 35 percent by weight aromatics. Generally, the aromatics content of a feedstock will range from about 5 percent by weight to about 80 percent by weight, more typically from about 10 percent by weight to about 70 percent by weight, and most typically from about 20 percent by weight to about 60 percent by weight.

Sulfur concentration in distillate fractions is generally a function of the high and low sulfur crude mix, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher sulfur distillate feedstock components are generally virgin distillates derived from high sulfur crude, coker distillates, and catalytic cycle oils from fluid catalytic cracking units processing relatively higher sulfur feedstocks. These distillate feedstock components can range as high as 2 percent by weight elemental sulfur but generally range from about 0.1 percent by weight to about 0.9 percent by weight elemental sulfur.

Nitrogen content of distillate fractions for hydrogenation is also generally a function of the nitrogen content of the crude oil, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher nitrogen distillate feedstocks are generally coker distillate and the catalytic cycle oils. These distillate feedstock components can have total nitrogen concentrations ranging as high as 2000 ppm, but generally range from about 5 ppm to about 900 ppm.

Typically, sulfur compounds in petroleum fractions include mercaptans, sulfides, and thiophenes such as substituted benzothiophenes and dibenzothiophenes. At first blush it might appear that heteroaromatic sulfur compounds could be selectively extracted based on some characteristic attributed only to these heteroaromatics. Even though the sulfur atom in these compounds has two, non-bonding pairs of electrons which would classify them as a Lewis base, this characteristic is still not sufficient for them to be

extracted by a Lewis acid. In other words, selective extraction of heteroaromatic sulfur compounds to achieve lower levels of sulfur requires greater difference in polarity between the sulfur-containing species and the hydrocarbons.

5 By means of the heterogeneous catalyzed oxidation according to this invention, it is possible to selectively convert these sulfur-containing species into, more polar, Lewis basic, oxygenated sulfur compounds such as sulfoxides and sulfones. A compound such as dimethylsulfide is a very non-polar molecule, whereas when oxidized, the molecule is very polar.
10 Accordingly, by selectively oxidizing heteroaromatic sulfides such as benzo- and dibenzothiophene found in a refinery streams, processes of the invention are able to selectively bring about a higher polarity characteristic to these heteroaromatic compounds. Where the polarity of these unwanted sulfur compounds is increased by means of heterogeneously catalyzed oxidation
15 according to this invention, they can be selectively separated by conventional solvent extraction, adsorption, washing or distillation processes while the bulk of the hydrocarbon stream is unaffected.

The process of the present invention also results in the oxidation of any nitrogen-containing species which can be simultaneously separated with the
20 sulfur-containing species by the conventional solvent extraction, adsorption, washing, or distillation processes mentioned above.

Other compounds which also have non-bonding pairs of electrons include amines. Heteroaromatic amines are also found in the same stream that the above sulfides are found. Amines are more basic than sulfides. The
25 lone pair of electrons functions as a Bronsted - Lowry base (proton acceptor) as well as a Lewis base (electron-donor). This pair of electrons on the atom makes it vulnerable to oxidation in manners similar to sulfides.

In one aspect, this invention provides a process for the production of refinery transportation fuel or blending components for refinery transportation
30 fuel, which includes: providing distillate feedstock comprising a mixture of hydrocarbons and sulfur-containing organic compounds and/or nitrogen-containing organic compounds, contacting the feedstock with an oxygen-containing gas in an oxidation zone in the presence of an oxidation catalyst wherein an oxygen-containing gas such as oxygen depleted air used. Because

oxygen depleted air can be used in the present invention, the concentration of oxygen can be less than about 21 vol. %. The oxygen-containing stream preferably should have an oxygen content of at least 0.01 vol. %. The gases can be supplied from air and inert diluents such as nitrogen if required. As
5 those skilled in the art readily recognize, certain compositions are explosive and the composition of oxygen-containing stream should be selected to avoid explosive regions. The oxygen-containing gas can be circulated in amounts ranging from 200 to 20,000 standard cubic feet per barrel of distillate.

The pressure in the oxidation zone can range from ambient to 3000
10 psig preferably from about 100 psig to about 400 psig, more preferably from about 150 psig to about 300 psig and most preferably from about 200 psig to about 300 psig.

The temperature in the oxidation zone can range from about 150°F to about 350°F, preferably from about 250°F to about 330°F.

15 The oxidation process of the present invention operates at a liquid hourly space velocity of from about 0.1 hr⁻¹ to about 100 hr⁻¹, preferably from about 0.2 hr⁻¹ to about 50 hr⁻¹, and most preferably from about 0.5 hr⁻¹ to about 10 hr⁻¹ for best results. Excessively high space velocities will result in reduced overall oxidation.

20 Generally, the oxidation process of the present invention begins with a distillate feedstock preheating step. The distillate feedstock is preheated in feed/effluent heat exchangers prior to entering a furnace for final preheating to a targeted reaction zone inlet temperature. The distillate feedstock can be contacted with an oxygen-containing stream prior to, during, and/or after
25 preheating.

Since the oxidation reaction is generally exothermic, interstage cooling, consisting of heat transfer devices between fixed bed reactors or between catalyst beds in the same reactor shell, can be employed. At least a portion of the heat generated from the oxidation process can often be profitably
30 recovered for use in the oxidation process. Where this heat recovery option is not available, cooling may be performed through cooling utilities such as cooling water or air, or through use of a quench stream injected directly into

the reactors. Two-stage processes can provide reduced temperature exotherm per reactor shell and provide better oxidation reactor temperature control.

5 The reaction zone effluent is generally cooled and the effluent stream is directed to a separator device to remove the oxygen-containing gas which can be recycled back to the process. The oxygen-containing gas purge rate is often controlled to maintain a minimum or maximum oxygen content in the gas passed to the reaction zone. Recycled oxygen-containing gas is generally compressed, supplemented if required, with "make-up" oxygen or oxygen-
10 containing gas (preferably air), and injected into the process for further oxidation.

The process of the present invention can be carried out in any sort of gas-liquid-solid reaction zone known to those skilled in the art. For instance, the reaction zone can consist of one or more fixed bed reactors. A fixed bed
15 reactor can also comprise a plurality of catalyst beds. Additionally the reaction zone can be a fluid bed reactor, slurry, or trickle bed reactor. The simplification implied by the use of a heterogeneous catalyst would facilitate a range of less conventional applications for the process of the present invention. For instance it is contemplated that the process of the invention can be carried out on skid
20 mounted units at terminals or pipelines, garage forecourts and on-board fuel cell containing vehicles where sulphur sensitive hydrocarbon reformers and fuels cells are employed.

The oxidation catalysts used in the present invention comprise a Group VIII metal component and a basic catalyst support. The preferred Group VIII
25 metals suitable for use in the present invention include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. The most preferred Group VIII metal is cobalt. These metals can be present in their elemental form or as oxides, or mixtures thereof. The metals are present in an amount ranging from 0.1 wt% to 50 wt.%, preferably about 2 wt% to about 20
30 wt. % and most preferably about 4 wt. % to about 12 wt. % based on the total catalyst weight.

The support component of the catalyst used in the process of the present invention is a basic support. Alkali oxides and alkaline earth oxides are the preferred supports, with MgO and CaO being most preferred.

5 The catalyst used in accordance with the present invention can be prepared by any of the standard methods of preparation known to those skilled in the art such as the precipitation method and the impregnation method.

More specifically, Group VIII component metals can be deposited or incorporated upon the support by impregnation employing heat-decomposable salts of the Group VIII metals or other methods known to those skilled in the art
10 such as ion-exchange, with impregnation methods being preferred. Suitable aqueous impregnation solutions include, but are not limited to cobalt nitrate, and nickel nitrate. Other impregnating solutions could include aqueous solutions of either metal oxalate, formate, propionate, acetate, chloride, carbonate or bicarbonate. Alternatively the solution may be organic when used
15 with metal compounds that are soluble in organic solvents e.g. metal acetylacetonates or metal naphthenates.

The oxidized sulfur-containing and/or oxidized nitrogen-containing compounds are then removed from the distillate via any conventional selective separation process such as adsorption, washing, distillation, and solvent
20 extraction.

Extractions can be carried out with solvents such as DMF, methanol, acetonitrile, sulfolane, and acetic acid. Suitable adsorbents include acidic alumina and silica. Alternatively, the oxidized sulfur-containing species will have boiling points greater than those in the feed and therefore can be readily
25 distilled from the distillate effluent. A suitable distillation cut point is equivalent to the temperature by which 90% of the feed sulphur compounds would boil is sufficient to reject the oxidized sulphur compounds as a residue from the product.

The process of the present invention also results in a distillate effluent a
30 relatively low TAN number. TAN is defined as mg KOH per gram of hydrocarbon sample required to neutralize any acids in the hydrocarbon sample. The TAN numbers of products, made in accordance with the process

of the present invention, are less than about 2.0, preferably less than about 1.0, and most preferably less than about 0.5. A high TAN number can result in a corrosive fuel.

5 The process of the present invention achieves desulfurization to a level below about less than 5 ppm wt. and achieves denitrogenation to a level of below about less than 10 ppm wt.

For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying figures and described below by way of examples of the
10 invention.

EXAMPLE 1

Table II below shows the results of carrying out the process of the present invention using a catalyst containing 8 wt. % Co based on the total catalyst weight, supported on MgO. The process was carried out in a batch
15 reactor at 200 psig, 900 rpm and 310 °F. The reactor used was a stirred, heated, 1 liter volume autoclave available from Autoclave Engineers having internal cooling coils and a means for continuous gas feed. The oxygen-containing gas having an oxygen content of 7 vol.% was added at a flow rate of 1200 standard cubic centimeters per minute. The reaction time was 5 hours.
20 The distillate feed had the composition set out in Table I below. The batch reactor contained 300 grams of distillate feed and 9 grams of catalyst.

FIGURE I plots the retention times in minutes for the sulfur-containing species signals in millivolts for a feedstock and an oxidation zone effluent stream shown in Table II, with the latter plotted below the feedstock. The
25 longer retention times indicate that the sulfur species have been converted to heavier species which are more readily removable from the effluent by a conventional downstream separation process.

30
Table I
Distillate Feed Composition
Analytical Tests

Oxygen (wt%)	0.10
Carbon (wt%)	87.02
Hydrogen (wt%)	12.80
Sulfur (ppm)	24
Nitrogen (ppm)	20
Spec. Grav.	0.8474
API Grav.	35.48
Aromatic Carbon (%)	20.20
 Hydrocarbon Type	
Saturates	58.7
Paraffins	26.1
Non-condensed cyclo Paraffins	20.7
Condensed Cycloparaffins, 2-rings	7.4
Condensed Cycloparaffins, 3-rings	4.5
Condensed Cycloparaffins, 4-rings	0.0
Condensed Cycloparaffins, 5-rings	0.0
 Aromatics	41.3
Monoaromatics (total)	38.0
Benzenes	20.7
Naphthenebenzenes	15.7
Dinaphthenebenzenes	1.6
Diaromatics (total)	3.3
Naphthalenes	3.3
Acenaphthenes, DBZfurans	0.0
Fluorenes	0.0
Triaromatics (total)	0.0
Phenanthrenes	0.0
Naphthenephenanthrenes	0.0
Tetraaromatics (total)	0.0
Pyrenes	0.0
Chrysenes	0.0
Pentaaromatics (total)	0.0
Perylenes	0.0
Dibenzanthracenes	0.0
Thiophenoaromatics (total)	0.0
Benzothiophenes	0.0
Dibenzothiophenes	0.0
Naphthobenzothiophenes	0.0
Unidentified	0.0
 GC Simulated distillation	
0.5 wt% (IBP)	239
1.0 wt%	262
5.0 wt%	330
10 wt%	360
20 wt%	395
30 wt%	421
40 wt%	442
50 wt%	458
60 wt%	476
70 wt%	490

80 wt%	509
90 wt%	525
95 wt%	536
99 wt%	550
99.5 wt% (FBP)	555

More specifically, Table II below shows the sulfur species present in both the distillate feedstock and the distillate effluent from the oxidation zone for a process carried out in accordance with the present invention as described

5 in this example.

Table II

Sample description total sulfur-ppmw	Feed 24.9	Product 29.6
Peak name or Retention time, min	ppmw-sulfur	ppmw-sulfur
H ₂ S	0	0
Mercaptans	0	0
Sulfides	0	0
Disulfides	0	0
Thiophene	0	0
C1 Thiophenes	0	0
C2 Thiophenes	0	0
C3 and C4 Thiophenes	0	0
C5 and C6 Thiophenes	1	0
C7 and C9 Thiophenes	2.87	0
Benzothiophene	0	0
C1 Benzothiophenes	1.07	0
C2 Benzothiophenes	2.46	0
C3 and C4 Benzothiophenes	17.41	6.0
Dibenzothiophene	0	0
17.18-18.85	0.09	16.11
19.04-20.04	0	7.14
20.13-20.58	0	0.39
>20.58	0	0

The feedstock in Table II is the same feedstock as set out in Table I, except
5 sulfur species were analyzed by a sulfur gas chromatograph.

As can be seen from the above table, the process of the present invention
achieves a shift in sulfur species to a heavier sulfur species which would result
in a desulfurization of about 90% achieving sulfur levels after a subsequent
separation step to below about 5 ppm.

10

EXAMPLE 2

Table III below shows the efficacy of the invention to reduce nitrogen
content in addition to sulfur content when carried out with a feed as described
in Table I. The runs were carried out in the same equipment described in
15 Example I except the oxidation reaction conditions where as otherwise set forth
in Table III. The oxidation reaction zone effluent was then extracted 3 times
using an 85% acetic acid solvent wherein the effluent to solvent volume ratio
was 2:1. The extractions were subsequently followed by 2 water washes.

20

TABLE III

Oxydesulfurization Catalyst	8% Co/MgO	8%Co/MgO
Reaction conditions		
Temperature, °F	310	265
Pressure, psig	200	200
7% oxygen gas flow rate, sccm	400	400
Rxn time, hr	5	1
stir speed, rpm	900	1400
Oxidized diesel sulfur, ppm-w	23	25
Oxidized diesel oxygen, wt%	2.01	0.16
Oxidized diesel TAN, mg KOH/g	1.38	0.10
Oxidized diesel nitrogen, ppm-w	11	11
acid-washed oxidized diesel sulfur, ppm-w	3	2
acid-washed oxidized diesel nitrogen, ppm-w	5	NA*

* Not Analyzed

5

EXAMPLE 3

Tables IV and V below show results of carrying out the process of the present invention using a fixed bed reactor.

TABLE IV

Oxydesulfurization Run

Catalyst	8% Co/MgO	8% Co/MgO	8% Co/MgO	8% Co/MgO
Diesel feed sulfur, ppm	25	25	25	25
Reaction conditions				
Temperature, °F	120	150	201	294
Pressure, psig	226	218	220	226
7% oxygen gas flow rate, sccm	250	250	250	250
Run time, hr	17	41	65	89
liquid hourly space velocity	0.5	0.5	0.5	0.5
Oxidized diesel sulfur, ppm-w	26	22	24	20
Oxidized diesel oxygen, wt. %	0.12	0.09	0.09	0.34
Oxidized diesel TAN, mg KOH/g	0.04	0.04	0.03	0.14
liquid product wt, g	139.02	148.47	136.98	150.31
liquid product mass balance, wt. %	96.50	103.06	95.09	104.34
acid-washed oxidized diesel sulfur, ppm-w	25	21	20	3
Final diesel recovery, wt. %	80.67	83.13	83.13	84.60

5

TABLE V

Oxydesulfurization Run

Catalyst	8% Co/MgO	8% Co/MgO	8% Co/MgO	8% Co/MgO
Diesel feed sulfur, ppm	25	25	25	25
Reaction conditions				
Temperature, °F	226	251	277	303
Pressure, psig	210	204	204	204
7% oxygen gas flow rate, sccm	250	250	250	250
Run time, hr	17	41	65	89
liquid hourly space velocity	1	1	1	1
Oxidized diesel sulfur, ppm-w	25	24	23	23
Oxidized diesel oxygen, wt. %	0.45	0.17	0.21	0.19
Oxidized diesel TAN, mg KOH/g	0.07	0.03	0.05	0.07
liquid product wt, g	155.62	142.88	141.6	139.5
liquid product mass balance, wt. %	108.03	98.22	95.49	96.84
acid-washed oxidized diesel sulfur, ppm-w	6	16	9	4
Final diesel recovery, wt. %	85.73	90.40	88.00	89.87